Defect Density Comparison of Detached versus Attached Bridgman-grown Germanium Crystals

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Introduction

During detached Bridgman growth, the melt meniscus at the tri-junction (gas-liquid-solid) is not in contact with the wall of the ampoule. This phenomenon, which is also called dewetting or necking, has been observed in recent years, mainly in microgravity experiments. Reviews about this growth-techinque, are given e.g. by Regel and Wilcox et al. [1] and Duffar et al. [2]. Under Earth conditions, it is more difficult to achieve detached Bridgman growth, because of the hydrostatic pressure, which counteracts the detachment mechanism.

Main factors and parameters promoting detachment:

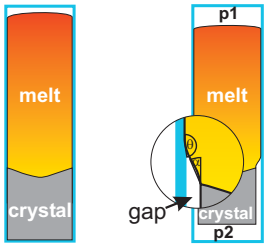
- **high contact angle θ between the crucible material and the melt**
  for germanium on a pBN substrate, a contact angle around 170° was measured [3]
- **high growth angle α**
  the growth angle for germanium is 7-13° [4]
- **pressure difference Δp between the melt meniscus and the top of the melt**
  pressure difference is possible through the use of the closed-bottom pBN container

Sufficient condition for detachment [2, 5]:

$\alpha + \theta \geq 180°$

α: growth angle; θ:wetting angle

Bridgman growth **Detached Bridgman**



Influence of additional pressure below the meniscus

p1=p2

The pressure above the melt (p1) and below the meniscus (p2) are the same. This is the case in the open-bottom pBN tube (compare the ampoule configuration on the upper right). Detachment can only occur if $\alpha+\theta \geq 180°$.

p1<p2

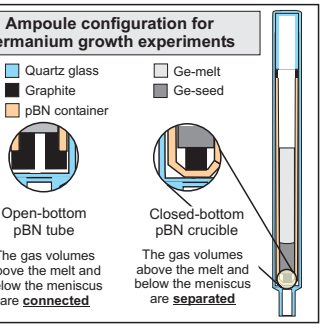
The pressure above the melt (p1) is lower than the pressure below the meniscus (p2). This promotes the detachment and can be achieved with the closed-bottom pBN crucible.

Experimental Setup

Germanium
(111)-orientation, Ga doped ($7 \cdot 10^{18}$ at/cm^3)
(110)-orientation, undoped
grown length: 45 - 60mm
diameter: 12mm

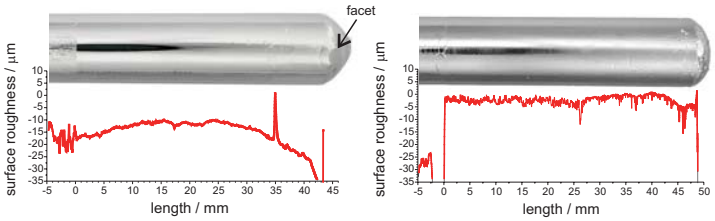
Furnaces
- Multizone Furnace UMC (24-zones)
  translation-free, zone programming (5mm/h)
  axial temperature gradient: 20-30K/cm
- 7-zone vacuum furnace
  with translation mechanism (5mm/h)
  axial temperature gradient: 25-35K/cm

Ampoule configuration for germanium growth experiments



Detached grown germanium crystal grown in closed-bottom crucible

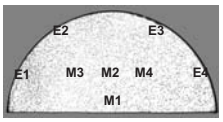
Attached grown germanium crystal grown in open-bottom tube



Micrographs from the surface

Figure above: All experiments performed in closed-bottom pBN crucibles resulted in single crystals that were mostly detached. One completely detached-grown crystal is shown together with an axial profilometer scan in the figure above. Three growth lines in the (111)-oriented crystal along the axial direction are an indication of single crystallinity (note also the facet at the top of the crystal). The average gap thickness in this crystal is 15µm. A contributing factor to the detachment in the closed-bottom configuration is a higher gas pressure below the meniscus compared to the pressure above the melt. This pressure difference might either be established by shrinking the gas volume around the seed at the beginning of the experiment, by the rejection of volatile impurities [6], or by a combination of both. For a reference condition, attached crystals were grown in open-bottom tubes. In addition to the profilometer measurements, the surface roughness was investigated by electron and optical microscopy.

To reveal the etch pit density, D-shaped, (111)-oriented radial wafers were prepared, and polished with 15µm, 9 µm, and 1 µm diamond paste and SYTON™. They were etched with the Billig etchant which is 12g KOH and 8g $K_3[Fe(CN)_6]$ dissolved in 100 ml H_2O at approximately 85°C. Four micrograph spots from the middle (M1-M4) and from the edge of the slices (E1-E4) were taken, the etch pits counted, and the average computed. The etched wafer on the right is from the seed crystal with a typical EPD ≈ $7 \cdot 10^3$ cm^{-2}.

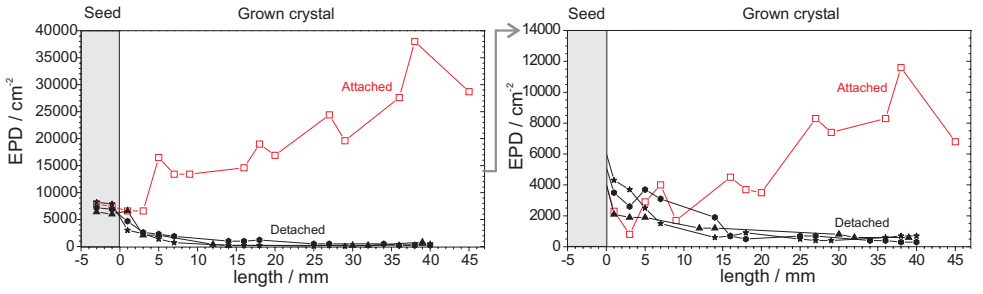


Etch Pit Density in Detached- and Attached-Grown Germanium crystals

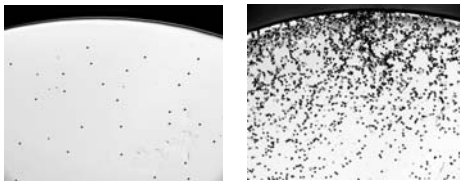
Detached grown crystals —★— UMC3 —●— UMC5 —▲— UMC7

Attached grown crystal —□— UMC6

along the Edge Note the **difference in scale** between the measurements along the edge and the middle **in the Middle**

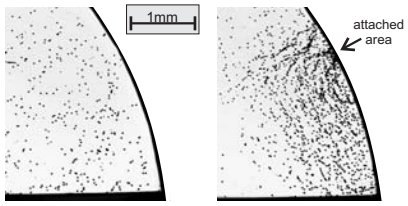


Completely detached grown crystal UMC7 — 1mm — Attached grown crystal UMC6



EPD ≈ 200cm^{-2} EPD ≈ $2 \cdot 10^4$cm^{-2}

Detached grown slice UMC2_9 — 1mm — Partly attached grown slice UMC2_10



Conclusions:

- Single germanium crystals were grown reproducibly
  - detached in closed-bottom pBN containers
  - attached in open-bottom pBN tubes
- No additional active pressure control was necessary for the detachment
- Typical gap thickness between the crystal and the ampoule wall is around 20µm
- Surface roughness and gap thickness was measured and investigated with profilometer and with optical and electron microscopy
- In the detached-grown samples, the EPD is reduced by two orders of magnitude compared to the attached sample. A lower EPD around 200 cm^{-2} is reached along the edge of the crystals and of approximately 500 cm^{-2} in the middle of the crystals.

Literature:
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Acknowledgement:
We are thankful to Ms. S. Gallop, Ms. P. Pettigrew, Mr. P. Carpenter and Ms. C. Cochrane for assistance in sample preparation and characterization and to Mr. C. Bahr and Mr. J. Quick for technical support. Helpful discussions with Dr. P. Dold and Prof. A. Cröll are appreciated. This work was supported by the NASA Physical Sciences Research Division.